

The recovery of accelerants in aqueous samples from fire debris using solid-phase microextraction (SPME)

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A popular method for the recovery of flammable and combustible liquid residues from fire debris is passive headspace concentration using activated charcoal strips (ACS) for the adsorption of the liquid residues followed by elution with carbon disulfide or other suitable solvent. In comparison to the ACS extraction, the adaptation of SPME to the headspace concentration of these residues from fire debris eliminates the use of solvents, decreases the time needed for analysis and raises the sensitivity of the extraction. Presently, we report the use of SPME for the rapid extraction of accelerants in aqueous solutions from fire debris requiring minimal sample handling. Extremely low quantities of pocket lighter fluid, gasoline and diesel fuel were directly extracted by SPME and their resulting gas chromatograms were accurately identified.

Une méthode fréquemment utilisée pour la recherche d'accélérateurs dans les résidus d'incendie est la concentration passive de l'espace de tête utilisant des bandes de charbon actif (ACS) pour l'adsorption des résidus liquides suivie d'une élution avec du sulfure de carbone ou tout autre solvant approprié. Par comparaison à l'extraction ACS, l'adaptation de la microextraction en phase solide (SPME) à la concentration de l'espace de tête élimine l'emploi de solvant, diminue le temps nécessaire à l'analyse et augmente la sensibilité de l'extraction. Présentement nous signalons l'utilisation de la SPME pour une extraction rapide d'accélérateurs de résidus d'incendie en solution aqueuse nécessitant une manipulation minimale de l'échantillon. De très petite quantité d'essence de briquet, d'essence et de diesel furent extraite directement par SPME et les chromatogrammes gazeux furent correctement identifiés.

Eine weit verbreitete Methode zur Gewinnung entzündlicher und brennbarer Flüssigkeitsreste aus Brandrückständen ist die passive Konzentration im Luftraum unter Anwendung von Aktivkohlefilmen (ACS) zur Adsorption der Flüssigkeitsrückstände und anschließender Elution mit Schwefelkohlenstoff oder einem anderen Lösungsmittel. Im Vergleich zur ACS-Extraktion macht der Einsatz der SPME (solid phase microextraction) zur Konzentration der Flüssigkeitsreste die Anwendung von Lösungsmitteln überflüssig, verringert die Analysenzeit und erhöht die Empfindlichkeit der Extraktion. Es wird über den Einsatz der SPME berichtet, um Brandbeschleuniger bei nur geringem Probenhandling aus wässrigen Lösungen von Brandrückständen zu extrahieren. Mit der SPME konnten noch äußerst geringe Mengen von Feuerzeugflüssigkeit, Benzin und Dieselmotorkraftstoff direkt extrahiert und gaschromatographisch eindeutig identifiziert werden.

Un conocido método para la recuperación de residuos de líquidos inflamables y combustibles, en restos de incendios, es la concentración pasiva en espacio de cabeza, utilizando tiras de carbón activo (ACS) para la adsorción de los residuos líquidos, seguido de elución con sulfuro de carbono o con otro disolvente adecuado. En comparación con la extracción ACS, la adaptación de SPME a la concentración del espacio de cabeza de estos residuos de restos de incendios, elimina el uso de disolventes, rebaja el tiempo de análisis y aumenta la sensibilidad de la extracción. Presentamos un informe del uso de SPME para la rápida extracción de acelerantes en soluciones acuosas de restos de incendios, requiriendo un manejo mínimo de la muestra. Cantidades extremadamente pequeñas de combustible de mecheros de bolsillo, gasolina y gasoil, fueron directamente extraídas mediante SPME y sus cromatogramas de gases resultantes, fueron exactamente identificados.

Key Words: Forensic science; Fire debris; Accelerants; Aqueous extraction; Solid-phase microextraction.

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Introduction

Solid-phase microextraction (SPME) was first reported by Pawliszyn [1] as a sensitive technique for the analysis of organic compounds which is easy to use, very fast and does not require the handling of any solvents [2]. SPME uses a sorbent-coated fibre to extract compounds for their subsequent thermal desorption directly into the injection port of a gas chromatograph. The advantages that SPME offers over traditional extraction techniques stems from the integration of the sampling, extraction, concentration and sample introduction into a single step. The use of SPME has since been applied to a variety of sample types for extraction from head space [3] and from solutions [4]. The use of SPME has been applied to the analysis of compounds of environmental interest from aqueous solutions [5,6,7], from soils [8], and even from animal tissue [9], as well as the analysis of contaminants in food [10,11]. The forensic applications have included the head space extraction of amphetamines from urine [12] and the head space extraction of flammable and ignitable liquid residues from fire debris [13,14]. The authors have demonstrated the first application of head space-SPME to the successful analysis of a wide range of accelerants, including gasoline in the presence of pyrolysis products in fire debris [14]. This paper reports the application of this technique to the analysis of a range of accelerants by their direct extraction from an aqueous solution. The range of accelerants is represented by a light petroleum distillate (LPD), gasoline and a heavy petroleum distillate (HPD). This technique enables a fire investigator to collect suspect water samples from a fire scene for the rapid laboratory analysis of accelerants present.

Materials and Methods

The three accelerants tested were the LPD Zippo pocket lighter fluid, Fina 87 octane gasoline, and the HPD diesel fuel.

The concentration methods published by ASTM [15–17] all involve the desorption of residues with a volatile solvent, typically carbon disulphide, followed by analysis by gas chromatography [18]. The advantages of head space-SPME over these concentration methods are reported elsewhere [13].

GC separations were performed on a Perkin Elmer 8420 gas chromatograph (Norwalk, Connecticut) using a 0.2 mm internal diameter x 30 m HP-1 column (Hewlett Packard, Wilmington, Delaware) with a 0.25 μm film thickness. The helium carrier gas flow rate was 1.0 ml/min. The injection port temperature was 220 °C and the detector temperature was 300 °C. The GC oven temperature was held at 35 °C initially for 2 minutes, then increased at a rate of 10 °C/min to 220 °C and held for 2 minutes, followed by a second temperature ramp of 30 °C/min to 300 °C, and finally held for 5.0 minutes. The GC was operated at a 50:1 split ratio for

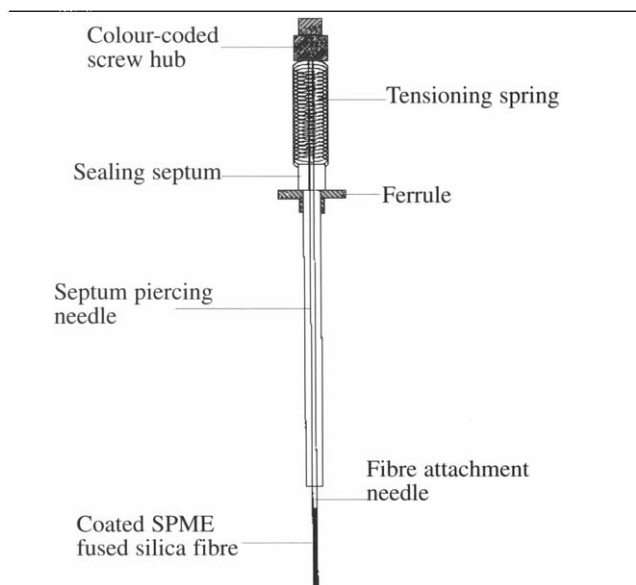


FIGURE 1 Diagram of SPME fibre assembly. (Reprinted with permission of Supelco, Inc., Bellefonte, PA 16823).

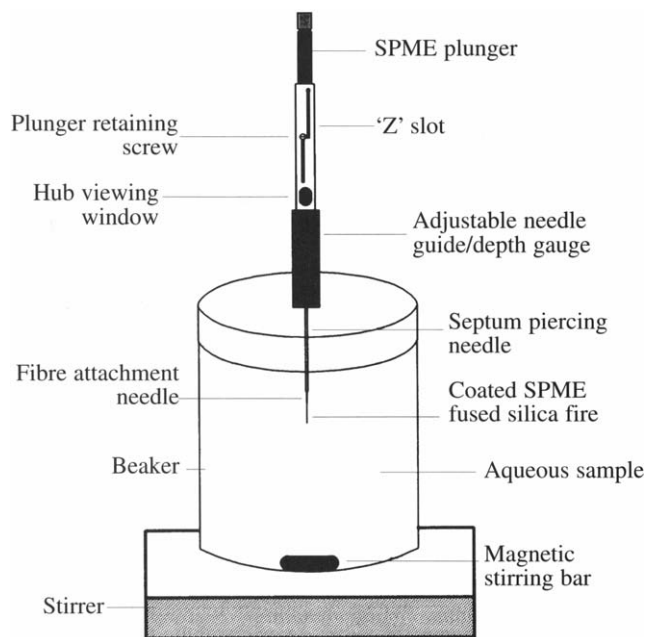


FIGURE 2 Diagram of SPME sample holder and experimental setup.

the neat (5% v/v in CS_2) analytes and in the splitless mode using a low volume (0.2 mm) injection port sleeve for the SPME desorptions.

The SPME sample holder (Supelco, Bellefonte, Pennsylvania) was placed above a beaker containing the aqueous solutions of the accelerants in a total volume of 100 ml. The SPME fibre detailed in Figure 1 containing a 100 μm film thickness polydimethylsiloxane sorbent phase was exposed to the solution for 20 minutes (Figure 2). The fibre was then retracted back into the SPME needle and inserted directly into the injection port of the gas chromatograph and the plunger depressed for ten seconds to desorb

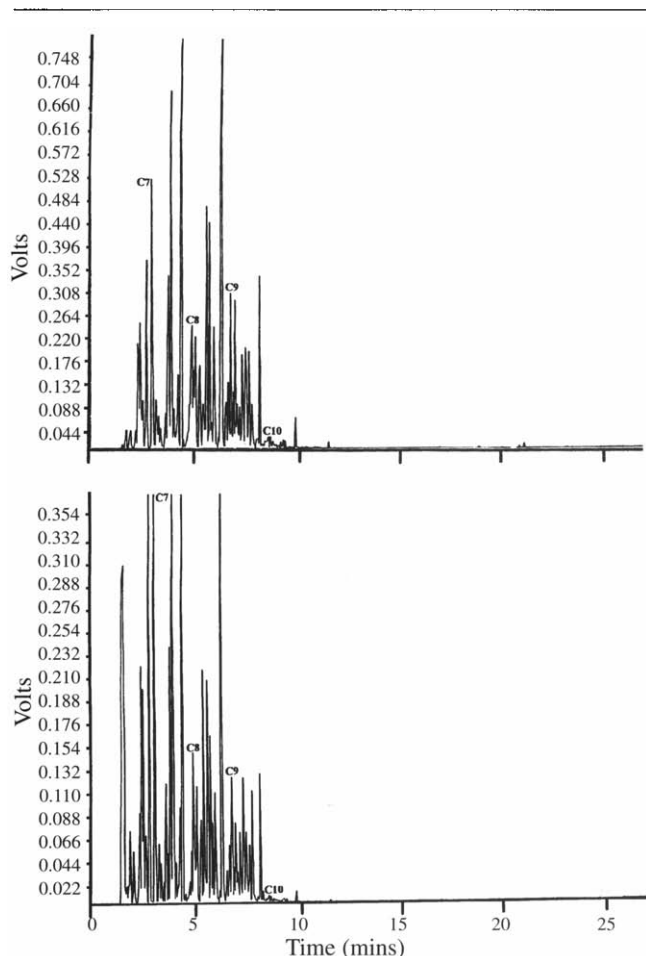


FIGURE 3 Chromatogram of SPME extract (top) and neat injection (bottom) of Zippo pocket lighter fluid with n-alkanes labelled and further peak identification given in Table 1.

TABLE 1 Peak identification for Figures 3, 4 and 5.

Peak	Compound	Peak	Compound
1	Carbon Disulphide	8	1,2,3 Trimethyl Benzene
2	Toluene	9	n-Butyl Benzene
3	Ethyl Benzene	10	Naphthalene
4	m & p-Xylene	11	2-Methyl Naphthalene
5	o-Xylene	12	1-Methyl Naphthalene
6	m & p-Ethyl Toluene	13	Pristane
7	1,2,4 Trimethyl Benzene	14	Phytane

the analytes into the GC. Injection was performed in the splitless mode with the split turned on six seconds after injection. (Note: In order to avoid the introduction of water into the column of the GC, it was sometimes necessary to remove water residue from the fibre by gently wiping the end of the metal shaft with a KimWipe.) The fibre assembly was cleaned between injections by allowing the fibre to remain in the heated injector of the GC for about five minutes after the splitter was turned on. Each SPME fibre can be reused for approximately 60 to 100 injections. The response from the GC flame ionization detector (FID) for selected peaks from the samples extracted using the SPME

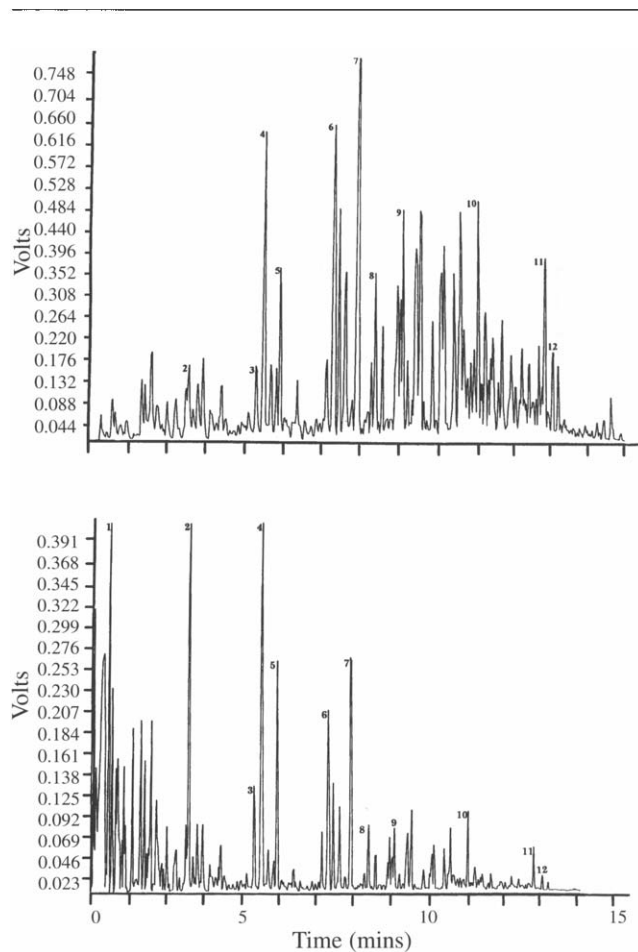


FIGURE 4 Chromatogram of SPME extract (top) and neat injection (bottom) of gasoline with peak identification given in Table 1.

method was measured and compared to the FID response for the samples that were extracted with hexane. The solvent extraction method used for this study is a modification to the solvent extraction method described in ASTM E 1386-90 (15). One hundred millilitres of aqueous solutions of accelerants with the same concentrations as in the SPME method were washed with 5 ml of hexane and the resulting extract was evaporated to 100 μ l for analysis with a 1 μ l injection into the GC.

Results

The resulting chromatograms obtained by the SPME extraction method and those obtained from the neat injections are compared in Figures 3, 4 and 5. Figures 3 and 4 illustrate the comparisons of extractions of 50 ppm aqueous solutions of a pocket lighter fluid and gasoline, respectively, to that of their neat injections. Figure 5 illustrates the comparison of an SPME extraction of a 500 ppb aqueous solution of diesel fuel to that of its neat injection. All of the same components are recovered by SPME, although the relative amounts are different for SPME compared to the neat injection. The equilibrium established between the sorbent coated SPME fibre and the aqueous sample appears to

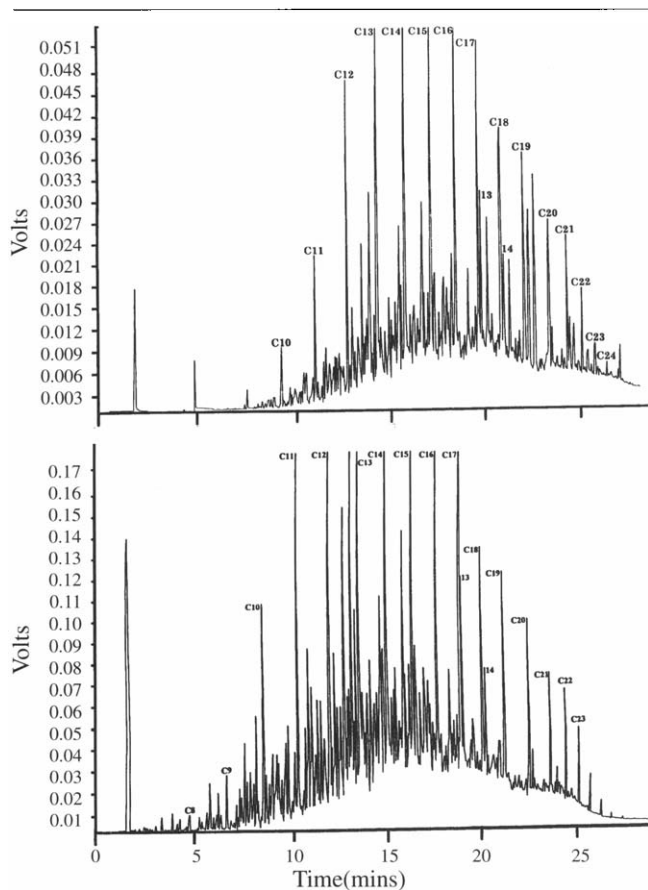


FIGURE 5 Chromatogram of SPME extract (top) and neat injection (bottom) of diesel fuel labelled and further peak identification given in Table 1.

favour the intermediate molecular weight (boiling) range components. Nevertheless, the chromatograms are identified as LPD for Figure 3, gasoline for Figure 4 or HPD for Figure 5 using the guidelines for classification published by ASTM [17]. The alkanes are labelled on the figures and Table 1 identifies the compounds labelled 1–14. Table 2 illustrates the comparison in FID response for SPME/hexane extractions for selected peaks in the LPD, gasoline and the HPD. An average increase of 8.9 and 32.0 times in sensitivity can be observed for 50 ppm LPD and 50 ppm gasoline solutions, respectively, for SPME vs the hexane extractions. The solvent extraction of the 500 ppb aqueous solution of diesel fuel did not produce an identifiable chromatogram by ASTM guidelines.

Discussion

The amount of liquid residues extracted by SPME is governed by the equilibrium which is established between the thin sorbent on the microextractor fibre and the aqueous medium. This allows for some concentration of the analytes while minimizing the potential of column overloading, which can be a problem with other concentration methods. Although the amount of analytes recovered by SPME is relatively small, there are no analyte losses due to sample

TABLE 2 Comparison in the FID response for SPME/hexane extractions for selected peaks in the LPD, gasoline and the HPD.

Analyte	Peak	FID response		
		SPME	Hexane	SPME/Hexane
Zippo lighter fluid	C7	.53	.048	11.0
	C8	.24	.036	6.7
	C9	.30	.033	9.1
Average				8.9
Gasoline	Ethyl benzene	.16	.013	12.3
	1,2,4 TMB	.75	.023	32.6
	Naphthalene	.51	.010	51.0
Average				32.0
Diesel fuel	C10	.010	—	—
	C17	.052	—	—
	C23	.010	—	—

handling or transfer and the entire extract is desorbed into the injection port of the GC for analysis, thus yielding high sensitivity. Compared to the established method of extraction for this type of sample (solvent extraction), the SPME technique described here increases the sensitivity, is less laborious, and does not require the use of any solvents.

The opinions or assertions contained herein are the private views of the authors and are not to be construed as reflecting the official views of the Metro-Dade Police Department.

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